

INVESTIGATION OF MORPHOLOGY AND MAGNETIC PROPERTIES OF COBALT NANOPARTICLES PREPARED USING MICROEMULSION TECHNIQUE

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ABSTRACT

Among many ferromagnetic materials cobalt nanoparticles with high coercivity and small grain size are one of the potential candidates having application in high-density storage media manufacturing. Magnetic cobalt nanoparticles have been synthesized via microemulsion technique to control the shape and size of high quality magnetic nanoparticles. In this technique, cetyltrimethylammonium bromide (CTAB) was added as surfactant to control the particle size. The morphology and magnetic properties have been characterized before and after annealing by X-ray diffraction, transmission electron microscopy and vibrating sample magnetometer. The hysteresis measurement of as prepared sample exhibits a coercivity of 27.26 Oe at room temperature. Annealing the sample at 400 °C enhance magnetic properties and change the crystal structure of particles from hcp to fcc.

Keywords: cobalt; nanoparticles; microemulsion; coercivity

INTRODUCTION

In recent years magnetic nanoparticles have constantly attracted great interest of many researchers because of their potential applications in biology, medical science, and electronic.

Single domain ferromagnetic alloy nanoparticles have tremendous potential in application of storage memory devices [1, 2]. Regards, two types of nanoparticles have been usually discussed: superparamagnetic particles (usually less than 10 nm) and ferromagnetic single-domain particles (10-50 nm). The uncoupled ferromagnetic single-domain particles have been used in composite permanent magnets. Particularly, magnetic nanosized materials have fundamental motivation because of their

application in ultrahigh-density magnetic recording systems, catalysis and electrochromic devices. Among magnetic materials, cobalt has intensive studies due to its multiple crystal structures (fcc, hcp and ϵ) and structure-dependent magnetic, and electronic properties. Pure cobalt nanoparticles (2-20 nm) are one of the great research interest due to unusual phenomena (Quantum effects) and industrial applications [3, 4]. The main difficulty in the use of small pure metals during experiment arises from their instability toward oxidation in air while the size gets smaller. This could be solved using a precious coating such as gold coating.

Cobalt nanoparticles have been prepared by various methods including thermal decomposition [5, 6], gas vapor condensation [7, 8], reverse microemulsion [9, 10], sol-gel [11], and precipitation method [12]. In this study we have applied reverse microemulsion to prepare the gold coated cobalt nanoparticles because of its ability to control the shape and size of the nanoparticles. Heat treatment of disordered cobalt increase the degree of long-range order in the cores, cause to change the direction of moments to easy direction of crystals and increase magnetocrystalline anisotropy, which is responsible for the increase in coercivity [13].

EXPERIMENTAL DETAILS

Materials and physical measurements

In this research metal, oil and reducing agent were purchased from across organics, co-surfactant from sigma-aldrich, and surfactant from R&M chemical and gold salt from alfa aesar. All materials were used without further purification. Distilled and deionized water was used throughout the experiment. X-ray diffraction (XRD) measurement were performed by Philips X-ray diffract-meter (model 7602 EA Almelo) at a scanning rate of 5 °/min in the 2θ range of 20° to 90°, using a monochromatized $\text{CuK}\alpha$ radiation ($\lambda=1.5418 \text{ \AA}$). The microstructure studies were performed using transmission electron microscopy (TEM) (Hitachi-7100) with an accelerating voltage of 120 kV. The magnetic measurement was carried out using vibrating sample magnetometer (VSM) (model Lakeshore, 7404 series) at room temperature.

Preparation of Nanoparticles

All syntheses were performed under argon gas. Nanometer size particles were synthesized using reverse micelles of cetyltrimethylammonium bromide (CTAB), using 1-butanol as the co-surfactant and octane as the oil phase [14, 15]. The aqueous solution containing the metal ions was added to this solution. The molar ratio of water to surfactant governs the size of the reverse micelle. For example, to form a reverse micelle of size 16 nm, the molar ratio of water to surfactant (CTAB) ($\omega = [\text{H}_2\text{O}]/[\text{CTAB}]$) must be adjusted to 16. The metal nanoparticles were formed within the reverse micelle by the reduction of metallic salt using sodium borohydride as a reducing agent. Sequential synthesis, afforded by reverse micelles was exploited for the synthesis of core-shell nanoparticles that metal located at the core surrendered with gold. Initially, two such solutions were prepared: one with metal salts (0.869 mmol per 5 g of aqueous solution) and another with reducing agent NaBH_4 (5.799 mmol per 5 g

of aqueous solution). Then, both solutions were mixed and stirred for two hours under argon gas. Excess of borohydride was used to suppress oxidation of cobalt by water. Furthermore, the micelles were expanded to accommodate a passivating gold shell by reducing 0.12 mmol aqueous gold salt. Nanoparticles were separated by doing centrifuge and then washing the particles with chloroform/methanol (1: 1) then leaving the product to dry at room temperature. The resulting powder is black in color. All solids were annealed at 400 °C for almost two hours under argon.

RESULTS AND DISCUSSION

The X-ray diffraction patterns show that the precipitate was a mixture of cobalt, gold and cobalt boride. The peaks in Figure 1a can be indexed to (111), (200), (220) and (311) plans of cubic gold (JCPDS: 89-3697). The XRD spectrum also showed the characteristic patterns of hcp metal cobalt, (002) with lattice parameter ratio $c/a=1.6$ (JCPDS: 89-4308) before annealing. Despite of XRD patterns revealed pure Co phase, no cobalt oxide phase was detected since we used particles gold coating. Reduction of cobalt (II) with borohydride is very complicated. Reduction of cobalt ions by borohydride may be caused the formation of various products among which cobalt metal was more produced. Furthermore, cobalt boride (Co_2B) plane of (411) with tetragonal structure (JCPDS: 89-1994) was observed in XRD data. The final product of microemulsion is very sensitive to the concentration of water in the system. With a high concentration of water, metal boride Co_2B particles may form instead of pure metal particles [16]. After annealing, the crystal structure of cobalt nanoparticles change from hcp to fcc with the lattice constant $a = 3.54$ regard to (111) plane (JCPDS: 15-0806), observed in $2\theta = 44^\circ$ (Figure 1b) [17]. In this figure, the plans of (312) and (411) are related to the Co_2B with the tetragonal structure. The width of peaks of Co nanoparticles after heat treatment becomes narrower than that of as prepared nanoparticles, indicating an increase in crystalline size after heat treatment. The crystalline size of cobalt coated with gold was 22 nm before annealing and 30 nm after annealing in 400 °C, calculated by Sherrer equation as follows:

$$D = \frac{0.9\lambda}{\beta \cos \theta}$$

where D is particle crystal size and λ is the wavelength, β is the full width at half maximum and θ is the position of the mean peak.

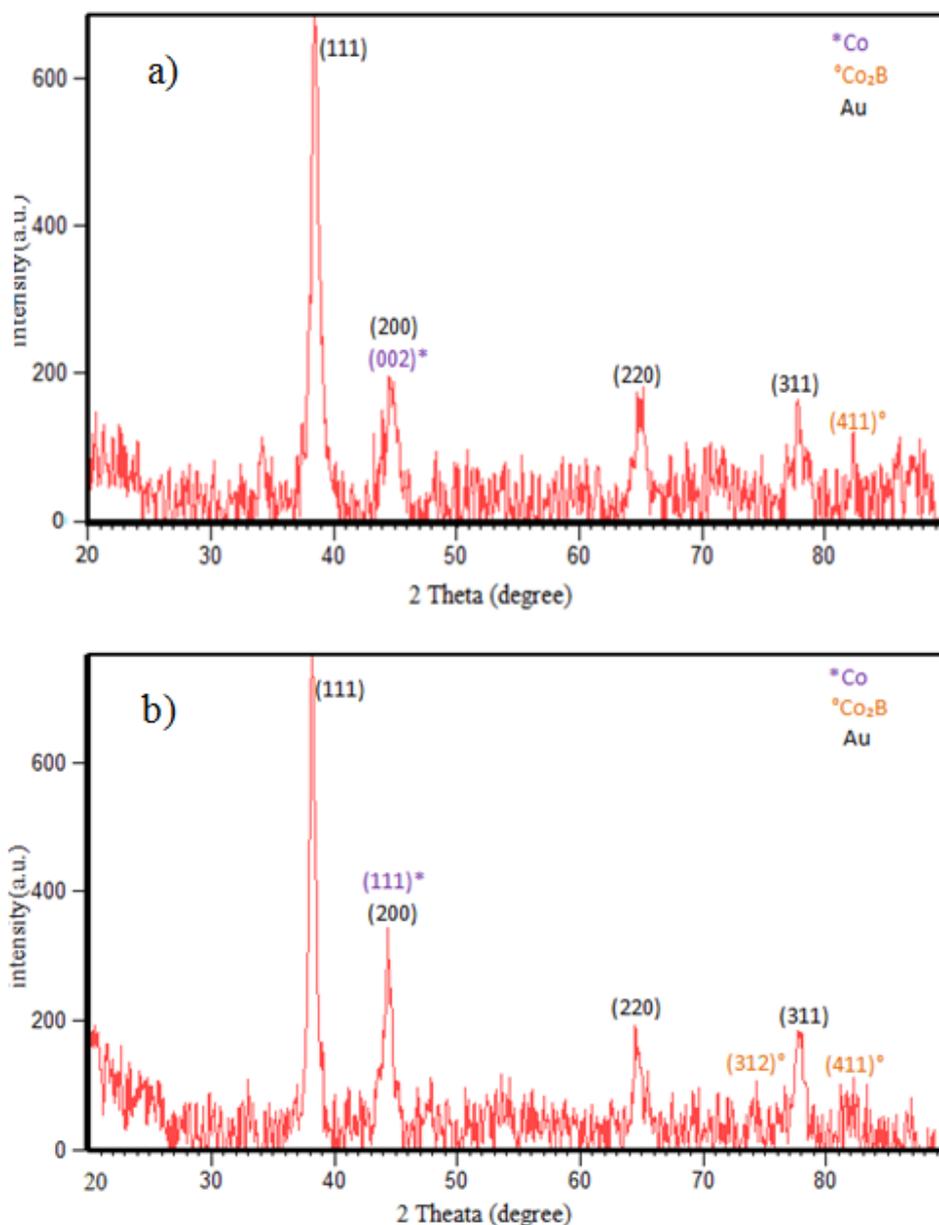


Figure 1: XRD spectrum of sample a) before annealing and b) after annealing

Figure 2 indicates TEM image of Co nanoparticles before and after annealing. Most of the Co nanoparticles were uniform and spherical in shape. Before annealing, most of the particles were agglomerated with core-shell structure but, after annealing at 400 °C they changed to a single spherical shape. The mean size of the particles before annealing was ~18 nm but after heat treatment increased to ~22 nm, compatible with XRD size measurements. After heat treatment, particle size increases slightly but do not fuse all together to grow a much larger size. Formation of spherical uniform nanocrystals in

reverse microemulsion highly depends on concentration of water to surfactant. The kind of surfactant used in this work controls the shape and size of micelles in solution. The results of XRD and TEM are in good agreement with our measurement while we expected the 16 nm water droplet size. Configuration of 18 nm particle size instead of 16 nm is because of particle gold coating.

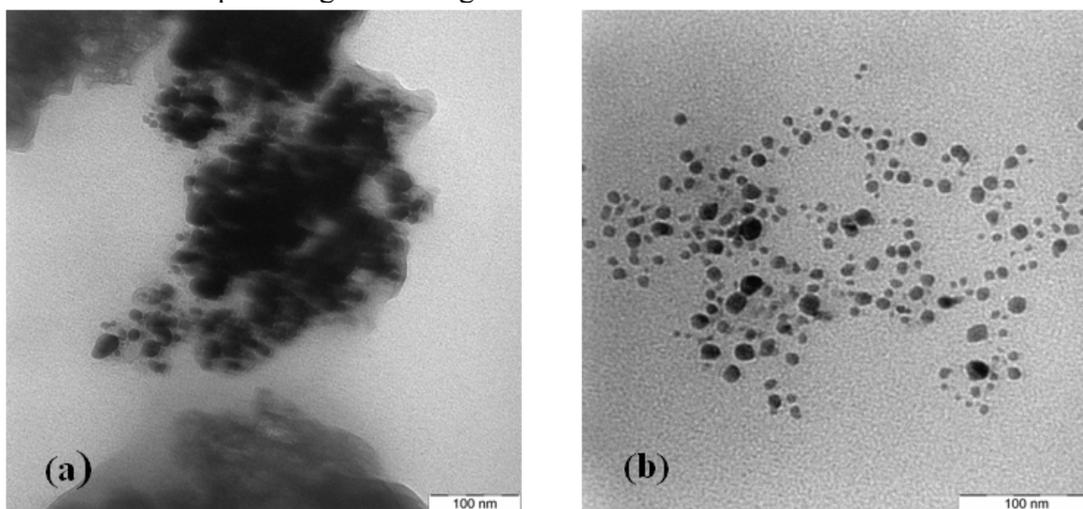


Figure 2: TEM image of sample (a) before annealing and (b) after annealing

The magnetic hysteresis loop measurements were performed on powdered nanoparticles sample at room temperature (300 K) with maximum applied magnetic field 12 kOe as shown in Figure 3. There was almost immeasurable coercivity for Co nanoparticles at room temperature, which was very typical behaviour for a soft magnet. VSM analysis indicated that the Co nanoparticles have a single domain structure and are superparamagnetic before annealing. The saturation magnetization, M_s , of the prepared sample was 6.92 emu/g. This was lower than the saturation magnetization after annealing (at 400 °C) 15.97 emu/g. The increase in magnetization is because of magnetic ordering between moments in domains. During heat treatment the moments will change their direction to the easy direction of crystals and enhance saturation magnetization [18]. Moreover, the coercivity after annealing increased from $H_C = 27.26$ Oe to 187.55 Oe at room temperature. The low values of M_s were obtained for the nanosize particles rather than bulk cobalt particles (~166 emu/g) [19] in both before and after annealing. The lower M_s and H_C of Co nanoparticles before annealing might be due to superparamagnetic behavior of nanoparticles documented by the hysteresis loop (Figure 3a). It showed that hysteresis disappeared with a little coercivity, indicating the absence of a long-range magnetic dipole–dipole interaction among the superparamagnetic cobalt nanoparticles before heat treatment. After annealing, the magnetization of the sample increased with a symmetric hysteresis loop (Figure 3b) showing a transition from superparamagnetic to ferromagnetic behavior. The magnetic properties of nanomaterials might be highly depends on sample shape, crystalline size and magnetization direction. Increasing in coercivity after annealing may be caused by

changing the superparamagnetic to ferromagnetic characteristics of cobalt nanoparticles [20].

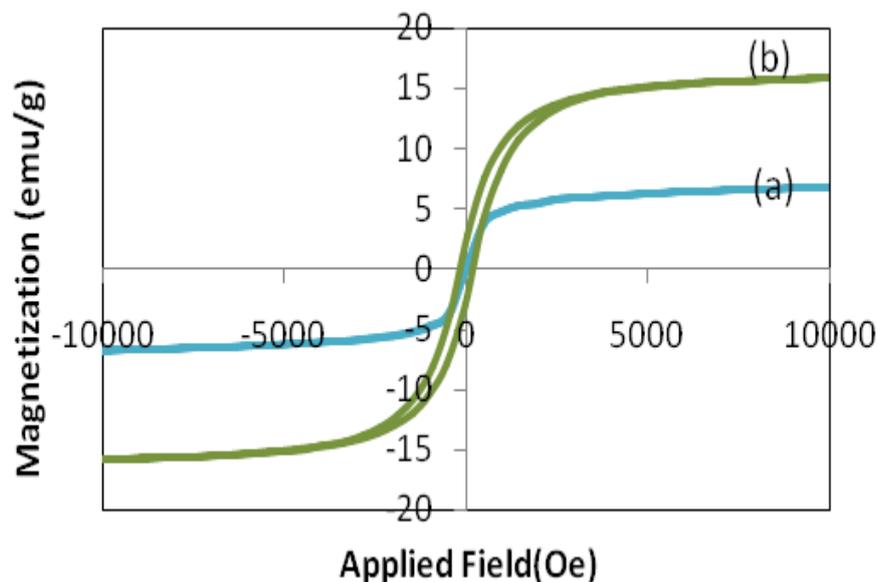


Figure 3: Magnetization versus applied field at 300 K for (a) Co before annealing (b) Co after annealing in 400 °C under Ar gas

CONCLUSION

This study showed that high annealing temperature is an effective factor to modify superparamagnetic single domain particles to ferromagnetic with a narrow size distribution as well as enhancing the intrinsic coercivity. Our data suggest that reverse microemulsion could be considered as a useful technique compared with other methods for synthesizing core-shell nanoparticles.

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